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PATENT

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Applicant: UWE GLATZEL ET AL.

Serial No.: 10/041,759 Group Art Unit: 1742

Filed: JANUARY 10, 2002 Examiner: JOHN P. SHEEHAN

Title: NICKEL-BASED ALLOY FOR PRODUCING COMPONENTS SOLIDIFIED IN SINGLE CRYSTAL FORM

DECLARATION OF THOMAS MACK UNDER 37 C.F.R. § 1.132

Commissioner for Patents
Washington, D.C. 20231

Sir:

I, Thomas Mack, do declare that:

1. I am a German resident and citizen and am fluent in the German language. I am also able to read and understand the English language.

2. My formal education includes attendance at the Technische Universität in Munich, Germany. In 1993, I received a Diploma Degree in Mechanical Engineering, which I understand to be equivalent to a Master of Science Degree of Mechanical Engineering in the United States. In 1998, I earned the PhD Degree in Mechanical Engineering at the Technische Universität in Munich, Germany.

3. Since 1998 until 2003, I have been employed by Daimler-Chrysler AG of Germany. I am employed in the department for Materials & Process Engineering at Daimler-Chrysler's subsidiary MTU Aero Engines GmbH in Munich. There I am responsible for development and approval of Ni-based single crystal materials, for development of casting processes and for assessment of high temperature materials, their physical and mechanical behavior and the influence of casting defects.

4. I have reviewed and am generally familiar with the subject matter of the above-identified U.S. Patent Application (hereinafter "'759 application). I have also reviewed, am familiar with, and understand Nguyen-Dinh et al., US Patent 4,935,072, and Bornstein et al., WO 93/24683.

5. As a practitioner of skill in the art, it is my opinion that the Nguyen-Dinh et. al and Bornstein et al. references do not teach or suggest all of the various limitations of the invention claimed in the above-titled application. In particular, neither Nguyen-Dinh et al. nor Bornstein et al. teach or suggests a low density alloy have a ratio of Re to W of 1.1. to 1.6. Additionally, neither Nguyen-Dinh et al. nor Bornstein et al. teach or suggests a low density alloy with a Re concentration of in-between 2.3% and 2.6%, nor do they teach or suggest a low density alloy with a W concentration of in-between 3.0% and 3.7%.

The refractory elements W and Re cause a significant increase in creep strength and temperature capability. On the other hand the addition of those elements has some detrimental effects such as density increase and thermodynamic instability which ends up in the formation of brittle topologically close packed (TCP) phases.

The above-titled application has several advantages over the prior art. These advantages include:

A. low density
B. high mechanical strength and ow creep tendency
C. high thermal stability and slow tendency to form TCP phases
D. improved heat treatment window
E. the absence of a low melting diffusion zone during coating

The main objective of the invention was to create an alloy with a low density and high mechanical strength. With regard to the low density we have reduced the alloy content of the refractory elements Ta, Mo, W and Re. Because of the influence of tungsten and rhenium which affect mainly the solid solution hardening of the alloy but increase density and raw material costs we have optimized the W- and Re-content on a low level with regard to the objectives high mechanical strength and low creep tendency.

Table 1 shows the most important LEK94 modifications SX1 to SX6 we have produced and additionally the composition of our experimental reference alloy SXref which is covered by the U.S. Patent Application 4,719,080. The proposed composition of LEK94 deviates from the patent W/O 93/24683, Bornstein et al. with regard to the Al-, Ta- and Mg-content and it deviates from the U.S Patent 4,935,072, Nguyen-Dinh et al. concerning the Cr-, Co-, Al- and Ta-content.

The experimental reference alloy SXref is also covered by the patent of Bornstein et al. and lies within the patent of Nguyen-Dinh et al. with a small exception. That exception is the Ti-content which is not relevant with regard of the alloys density.

Table 1: Composition, density and c_W/c_{Re}-ratio for the LEK94 invention, the experimental alloys including the benchmark alloy SXref and the alloys according to patents of Bornstein et al. and Nguyen et al.

	Composition in wt.-%													density	c_W/c_{Re}
	Cr	Co	Mo	W	Re	Al	Ti	Ta	Hf	Ni	Ru	C	Mg	g/cm³	-
LEK94															
low	5,8	7,2	1,7	3,0	2,3	6,2	0,9	2,0	0,05	70,9	0,0	0,0	0,0000	8,16	1,30
high	6,4	7,8	2,3	3,7	2,6	6,8	1,1	2,6	0,15	66,6	0,0	0,0	0,0000	8,11	1,42
nom	6,1	7,5	2,0	3,4	2,5	6,5	1,0	2,3	0,10	68,7	0,0	0,0	0,0000	8,14	1,37
Experimental alloys															
SX1-A	5,86	7,29	1,88	3,53	1,92	6,36	0,93	2,18	0,05	70,0	0,0	0,0	0,0000	8,15	1,84
SX1-B	5,82	7,26	1,86	3,50	2,12	6,22	0,94	2,15	0,06	70,1	0,0	0,0	0,0000	8,17	1,65
SX1-C	5,80	7,23	1,87	3,50	2,18	6,34	0,92	2,17	0,05	69,9	0,0	0,0	0,0000	8,16	1,61
SX2	5,69	7,2	1,92	3,87	2,95	6,23	0,95	2,26	0,11	68,8	0,0	0,0	0,0000	8,21	1,31
SX3	5,83	7,35	1,96	3,07	2,37	6,42	0,98	2,28	0,10	69,6	0,0	0,0	0,0000	8,14	1,30
SX4	5,75	7,27	1,95	3,05	2,76	6,35	0,96	2,27	0,11	69,5	0,0	0,0	0,0000	8,17	1,11
SX5	5,77	7,3	1,95	3,3	2,57	6,35	0,97	2,28	0,11	69,4	0,0	0,0	0,0000	8,17	1,28
SX6	5,82	7,33	1,96	3,56	2,33	6,39	0,97	2,28	0,11	69,3	0,0	0,0	0,0000	8,16	1,53
Sxref	5,0	10,0	1,9	5,9	3,0	5,7	0,0	8,7	0,1	59,7	0,0	0,0	0,0000	8,55	1,97
Bornstein et al.															
low	1,0	2,0	0,0	3,0	0,0	4,5	0,0	2,5	0,0	87,0	0,0	0,0	0,0005	8,45	-
high	12,0	12,0	2,5	10,0	8,0	6,5	2,0	13,0	0,5	33,4	0,0	0,1	0,0200	8,57	1,25
nom	5,0	10,0	1,9	5,9	3,0	5,7	0,0	8,7	0,1	59,7	0,0	0,0	0,0040	8,56	1,97
Nguyen-Dinh et al.															
low	4,0	8,0	1,0	3,0	1,8	5,6	0,5	7,7	0,1	68,3	0,0	0,0	0,0005	8,40	1,67
high	6,0	12,0	2,5	5,0	2,9	6,0	1,5	8,2	0,2	53,2	2,5	0,0	0,0000	8,41	1,71
nom	5,2	10,1	2,0	5,0	2,9	5,5	0,8	7,7	0,1	60,7	0,0	0,0	0,0000	8,48	1,72
	Mo + W + Re = 8,4 - 10,4 and Al + Ti + Ta = 13,8 - 15,7, free of V, C, B, Zr														

6. We have performed several investigations and experiments to compare the properties of the claimed alloy of the above titled invention with the disclosures in Nguyen-Dinh et al. and Bornstein et al.. In the following the experimental results are structured according to the above mentioned advantages:

A. Low Density Alloy

An aim was to find an optimum composition of a nickel base superalloy regarding a minimum density with maximum creep resistance. Several single crystal samples with varying composition and very small disorientation from the ideal <100> orientation have been produced. The measured densities of these alloys are given in Figure 1.

The reduction of tungsten and rhenium content has a significant impact on the density of the alloy: the lower the Re- and W-content the lower the density. For the cited references Bornstein et al. and Nguyen-Dinh et al. the density of their proposed alloys does not fall below 8.40 g/cm³ (see table 1). Thus LEK94 has a at least 3 % lower density which makes a significant weight impact: the reduced weight of turbine blades leads to a reduction in weight for the turbine disk and for the containment especially for high rotating low pressure turbines. As an additional benefit the raw material cost is reduced due to the high Re material costs.

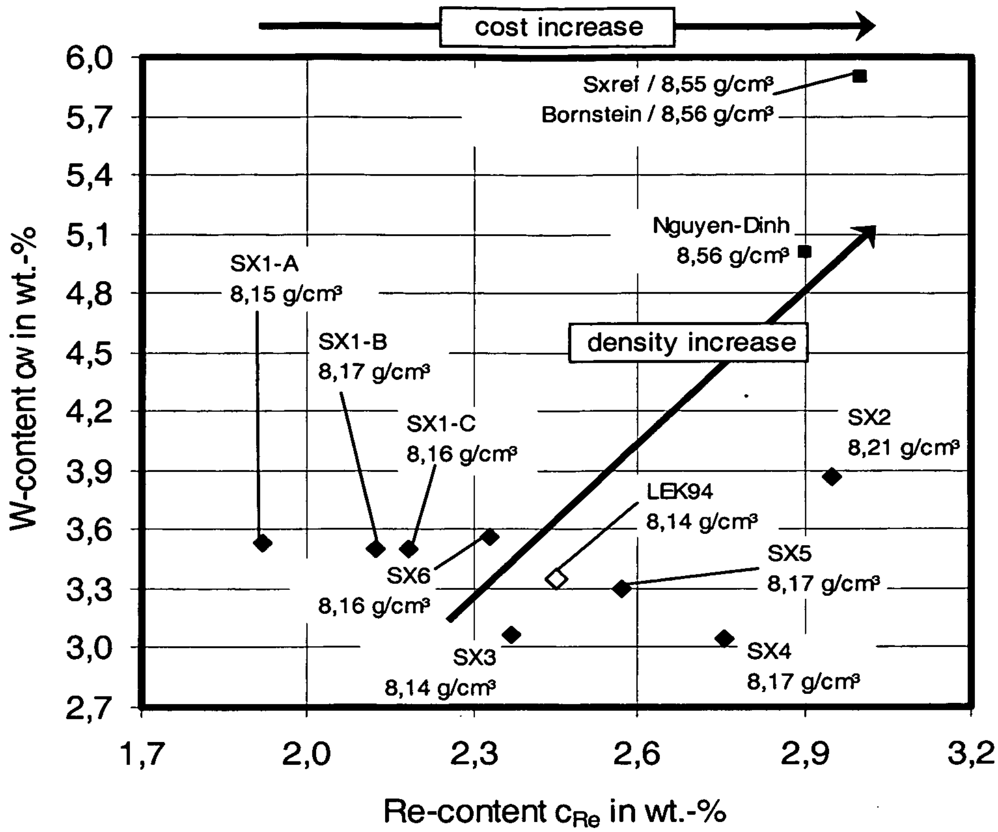

Figure 1: Variation in alloy composition and density of the experimental and reference alloys at nominal composition

B. Alloy with High Mechanical Strength and Low Creep Tendency

In most studies the creep strength is rated by the time to failure. Since airfoils are restricted in creep strain by the turbine surroundings we used the time to reach 1% or 2% strain as an indication for creep strength.

The influence of the alloying element Re on the creep strength (time to reach 2 % plastic strain) at 980 °C/230 MPa is shown in Figure 2. For the experimental alloys the W-content is in-between 3 and 3.9 wt.-%. A decrease of the Re-content below 2.3 wt.-% causes a significant decrease in creep strength. Therefore 2.3 wt.-% Re is a kind of threshold value described in claim 1 of our patent. Both cited references, Bornstein et al. and Nguyen-Dinh et al., include Re-contents below 2.3 wt.-% and do not consider the threshold at 2.3 wt-%.

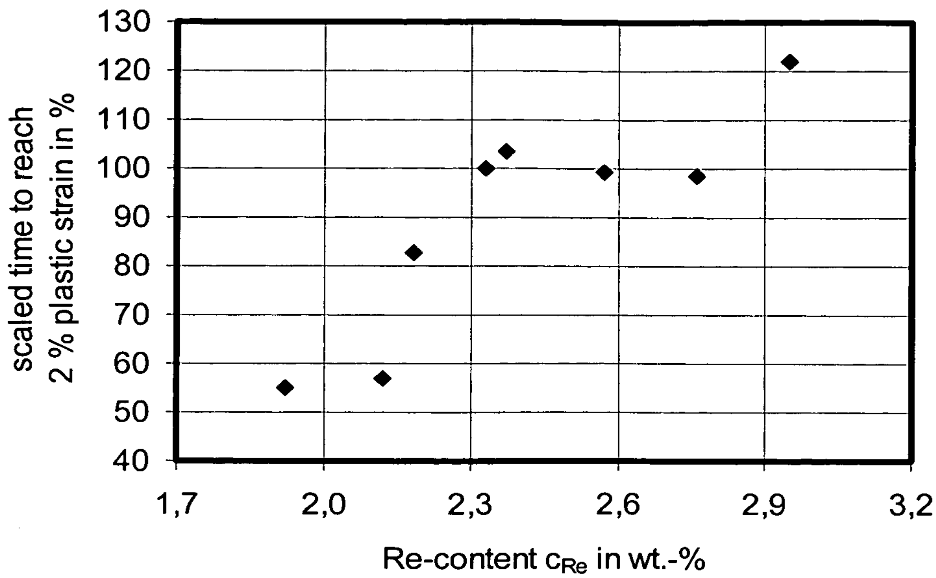

Figure 2: Influence of Re-content on creep strength; the W-content of the alloys investigated is between 3 and 3.9 wt.-%

Figure 3 shows the time to reach 1% or 2% strain relative to the time to reach these strains for alloy SX2 in a creep experiment. A constant stress of 500 MPa was applied at a temperature of 850°C. We observed a steady increase in time to reach 1% or 2% strain if the W and Re content is increased. However the influence of W on creep strength is higher than the influence of Re as indicated by the arrow in direction of increasing creep strength. This arrow points into a direction of $c_W : c_{Re} = 2 : 1$.

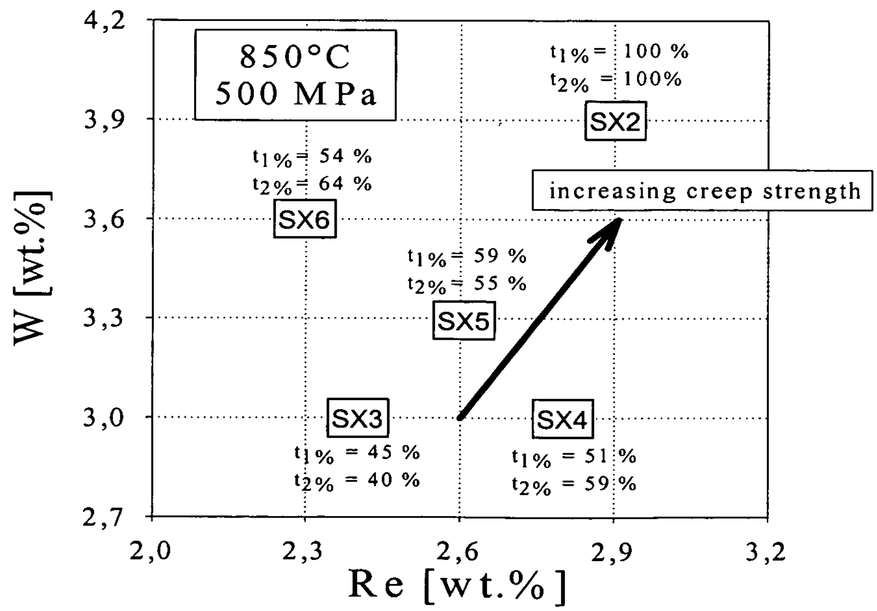

Figure 3: Time to reach 1% ($t_{1\%}$) or 2% ($t_{2\%}$) strain in a creep experiment with 500 MPa stress at a temperature of 850 °C related to alloy SX2, the arrow indicates the direction of increasing creep strength

The scaled creep strength of the experimental reference alloy SXref is 160 % for time to reach 1 % plastic strain $t_{1\%}$ and 110 % for time to reach 2 % plastic strain $t_{2\%}$. This strength increase is mainly due to the relatively large sum of refractory elements W + Re + Ta = 18,6 of SXref.

Figure 4 shows the creep properties of the experimental alloys at a temperature of 980°C and 230 MPa. A maximum strength is obtained for alloys with tungsten to rhenium concentration ratio of about 1.33 as indicated in Figure 5.

The scaled creep strength of the experimental reference alloy SXref is $t_{1\%}$ = 254 % an $t_{2\%}$ = 281 %. Due to its high content of tungsten SXref does not follow the correlation described in Figure 5.

Using the traditional creep strength criterion of time to failure (t_B), the creep strength at an even higher temperature of 1100°C is determined only by the sum in concentration of elements with low diffusion coefficients, in our case the elements W and Re. However, taking the time to reach 1% as a creep strength criterion a similar behavior compared to 850°C is determined. Tungsten has a stronger influence than rhenium, see Figure 6. The scaled creep strength for the experimental reference alloy SXref is $t_{1\%}$ = 135 % and t_B = 106 %.

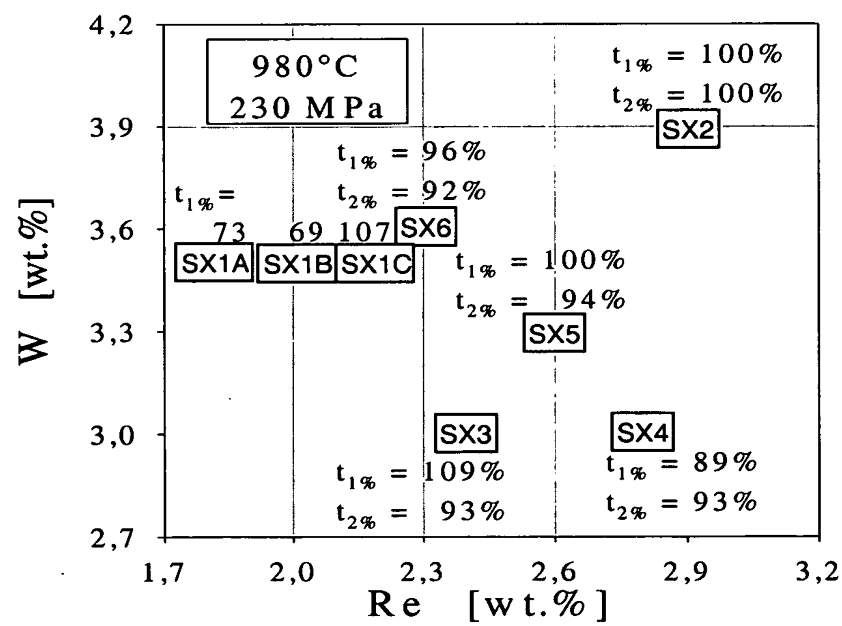

Figure 4: Time to reach 1% ($t_{1\%}$) or 2% ($t_{2\%}$) strain in a creep experiment with 230 MPa stress at a temperature of 980°C related to alloy SX2

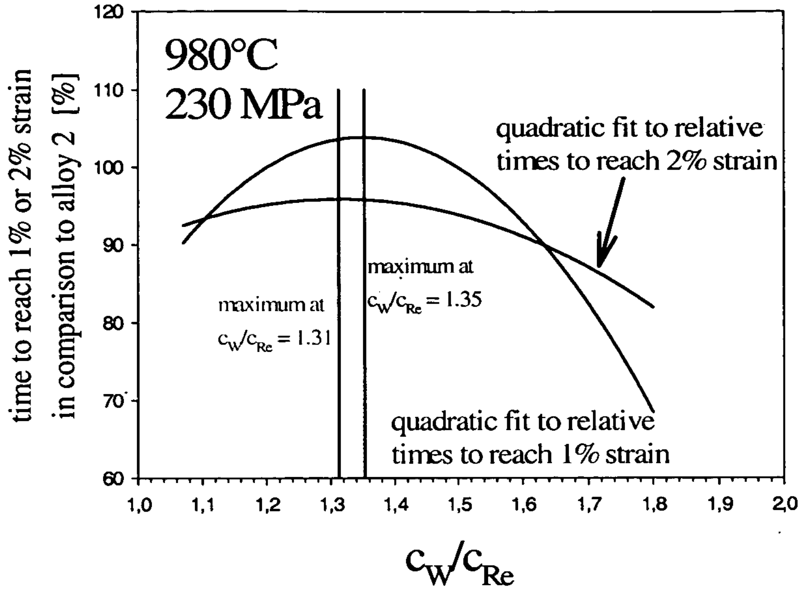

Figure 5: Estimation of optimum tungsten to rhenium concentration according to creep results obtained at 980°C and 230 MPa

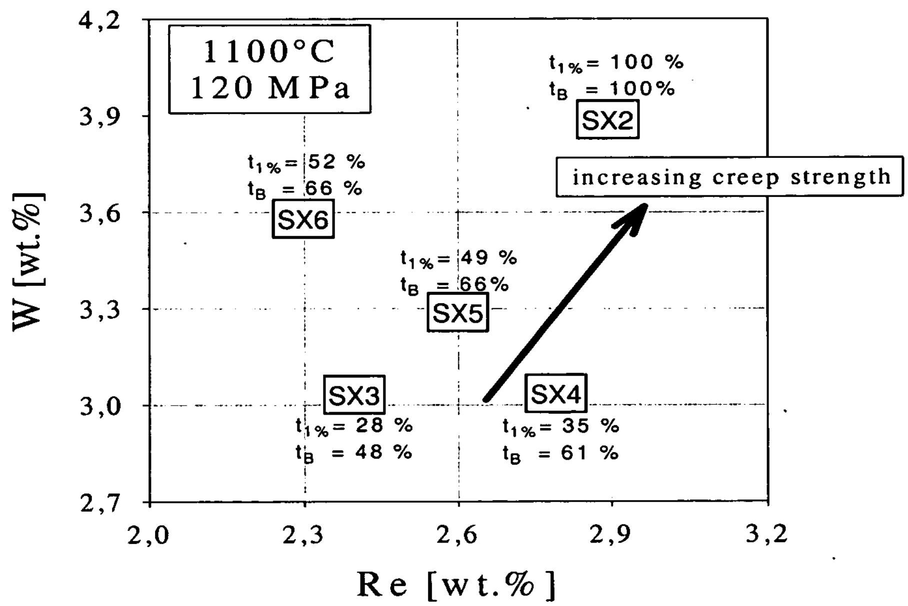

Figure 6: Time to reach 1% strain ($t_{1\%}$) and time to rupture (t_B) in a creep experiment with 120 MPa stress at a temperature of 1100°C related to alloy SX2

Taking all the creep measurements given above into account we come to the following conclusions:

- A concentration ratio c_W/c_{Re} of about 1.33 is an optimum.
- The rhenium concentration should not be reduced below 2.2 wt.%. This results from creep experiments carried out at 980°C.
- In the low temperature regime (850°C) and in the high temperature regime (1100°C) two weight units of Re can be replaced by one weight unit of W leading to the same creep properties with a reduction in specific density and alloy costs.

C. High Thermal Stability and Slow Tendency to Form TCP Phases

It is well known from literature that the high melting point elements W, Re and Ta are prominent elements which form undesirable topologically closed packed (TCP) phases, see for example:

[1] C.T. Sims, Superalloys II, ed. C.T. Sims et al., TMS, Warrendale, PA (1987) 217.

[2] R. Darolia, D.F. Lahrman, R.D. Field, Superalloys 1988, ed. S. Reichmann et al., TMS, Warrendale, PA (1988) 255.

[3] M. Simonetti, P. Caron, Mat. Sci. Eng. A 254 (1998) 1.

[4] C.M.F. Rae, R.C. Reed, Acta mat. 49 (2001) 4113.

[5] W.S. Walston, J.C. Schaeffer, W.H. Murphy, Superalloys 1996, ed. R.D. Kissinger et al., TMS, Warrendale, PA (1996) 9.

[6] W.S. Walston, K.S. O'Hara, E.W. Ross, T.M. Pollock, W.H. Murphy, Superalloys 1996, ed. R.D. Kissinger et al., TMS, Warrendale, PA (1996) 27.

To demonstrate the susceptibility to TCP-phase formation a LEK94-specimen and a specimen of the experimental reference alloy SXref were exposed at 1100 °C for 250 h. Both alloys exhibit TCP-phases adjacent to the coating. Furthermore the SXref alloy forms needle phases even in the bulk material (Figure 9). Due to the optimized and balanced W- and Re-content and the low content of tantalum the LEK94-alloy is free of the undesirable TCP needles.

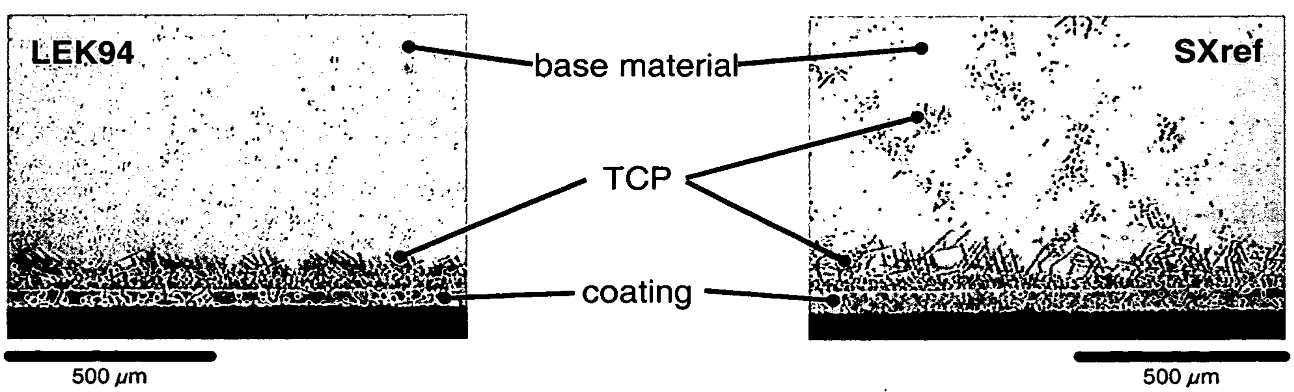

Figure 9: Influence of exposure at 1100 °C (250 h) on TCP-phase formation in Re-containing, coated superalloys LEK94 and SXref

D. Improved Heat Treatment Window

Beneath a good castability of an alloy the solution heat treatment window is another important criterion for an alloy. A large heat treatment window allows to fully solutioning the alloy without the risk of incipient melting and lowers the risk of recrystallization.

LEK94 has a relatively wide solutioning heat treatment window from 1285 °C where all γ'-phases are dissolved, to 1345 °C, where incipient melting starts. The experimental reference alloy, which has a comparable good castability, has a reduced heat treatment window of 1305 °C to 1340 °C.

E. Absence of a Low Melting Diffusion Zone after Coating

The incipient melting of the diffusion zone of an aluminide-coating depends on the chemical composition and on the geometry. Reducing the radius of the part decreases the melting temperature. The absence of a low melting diffusion zone and the improved behavior of the alloy in a coated condition were shown with two blades, one blade was cast in LEK94 with nominal composition and the other blade was cast in the reference material SXref. Both airfoils were aluminide-coated and thereafter aged at 1290 °C for 0.5 hours. Figure 8 shows the leading and trailing edges of both airfoils. The SXref-blade exhibits a melting of the diffusion zone and a lift-off of the coating at the trailing as well as the leading edge. The LEK94-blade doesn't show any melted diffusion zone, although the radii of the edges are smaller than the radii of the blade made of SXref.

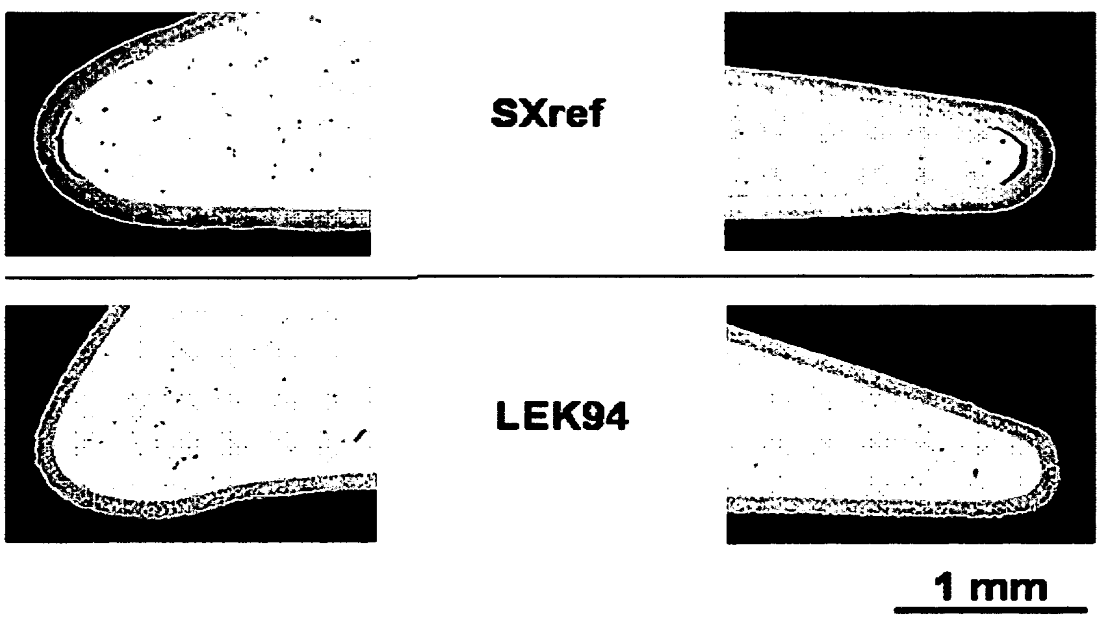

Figure 8: Leading and trailing edges of aluminide-coated airfoils cast in SXref-alloy and LEK94 after annealing at 1290 °C for 0.5 hours; the SXref-airfoil shows a melted diffusion zone and a lift-off of the coating whereas the LEK94-airfoil doesn't

7. Therefore, based on the data presented above, it is my opinion that alloys of the claimed invention provide unexpectedly superior properties over the broad range of alloys disclosed in Nguyen-Dinh et al. and Bornstein et al.. As one can see from Table 1 previous inventions did not optimiz their results with respect to minimize the W and Re concentration. The invention described here specifically optimizes a nickel based superalloy with respect to good creep properties, reduced tendency to form TCP phases and especially to a low density. The low density is the main focus which has to be taken into account when, for example, the creep properties of LEK94 are compared to other alloys. Therefore the low density is even considered in the name of this alloy: LEK94 means "**L**eichte **E**in**K**ristalllegierung" (low weight single crystal alloy). It is further my opinion, based on the data presented above, that the unexpectedly superior properties could not found by routine optimization, as the importance of considering the threshold at 2.3 wt.-% Re and maintaining a ratio between Re and W of 1.1 to 1.6 is not disclosed in the prior art.

8. I declare that the preceding statements which are made of my own knowledge are true and that the preceding statements which are made on information and belief are believed to be true. I am aware that willful false statements and the like are punishable by fine or imprisonment or both under Section 1001 of Title 18 of the United States Code and may jeopardize the validity of the application or any patent issuing thereon.

December 17, 2003 Thomas